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Water Quality Monitoring of Springs Discharging from Mississippian Bedrock Aquifers in Indiana
– Enhancing IGWS Contributions to the National Groundwater Monitoring Network

Authors:

Tracy Branam

1001 E. 10th St.

Bloomington, IN 47405

Phone: (812) 855-8390

Email: tbranam@indiana.edu

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Monitoring the Mississippian Aquifer of Indiana through the use of natural springs

Summary

This project was designed to monitor the water quality of the Mississippian Aquifer by sampling several springs flowing from Mississippian bedrock throughout the southwest/southern regions of Indiana, where such bedrock is exposed at the surface. This occurs primarily in two physiographic provinces of Indiana: the Mitchell Plateau and the Crawford Uplands. The Mitchell Plateau is dominated by carbonate bedrock at the surface. It is characterized by prevalent mantled karst features associated with chemical and physical erosion of carbonate rocks, including sinkholes, caves, sinking streams, blind valleys, and springs. The Crawford Uplands contain a mix of clastic and carbonate bedrock units, producing ridge and valley topography with sinkholes present where carbonate units comprise the surface bedrock, with caves and springs occurring in lower elevation regions, most notably at the base of ridges and in valley floors. In addition to karst and cave springs, the Crawford Uplands contain springs formed at stratigraphic contacts and in fractures.

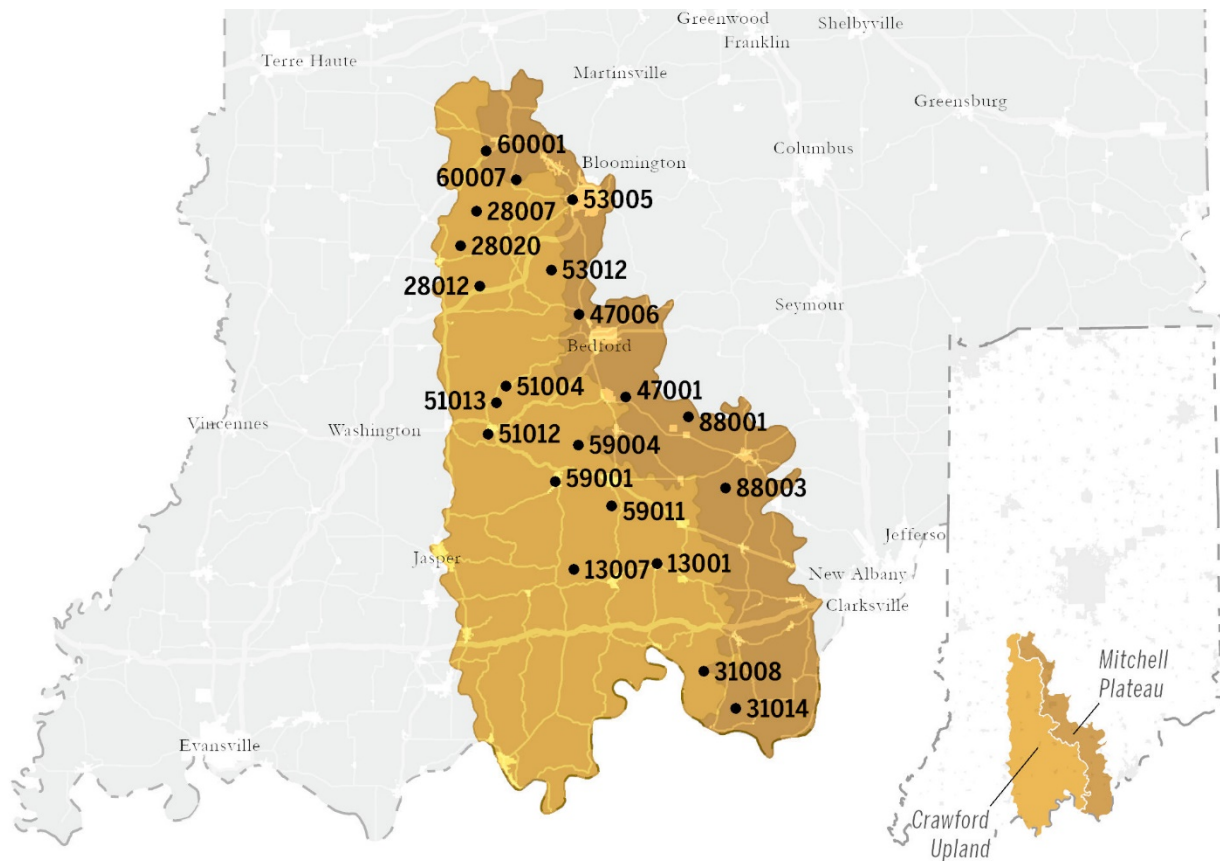


Figure 1. Map of physiographic provinces involved in the study with spring locations.

Of primary importance was the selection of perennial springs to ensure that water collected was issuing from the bedrock aquifer and not surface water recharge. To further guarantee that only bedrock aquifer water was being characterized, sampling only occurred during the dry season for the state, generally from August through October. This is the first network of water quality monitoring sites for the Mississippian Aquifer System in Indiana. Having a large number of sites is important for meaningful data collection because of the variable nature of spring recharge and groundwater migration in karst-dominated regions. This is evident from the large variability in spring discharge rates and major ion chemistry from the sites being monitored.

A total of 21 springs were sampled, spaced over nine counties, covering a linear distance of approximately **90.29 [measured]** miles from the northernmost spring to the southernmost spring, and all of the springs within an approximate area of over **1,127.31 [measured]** square miles.

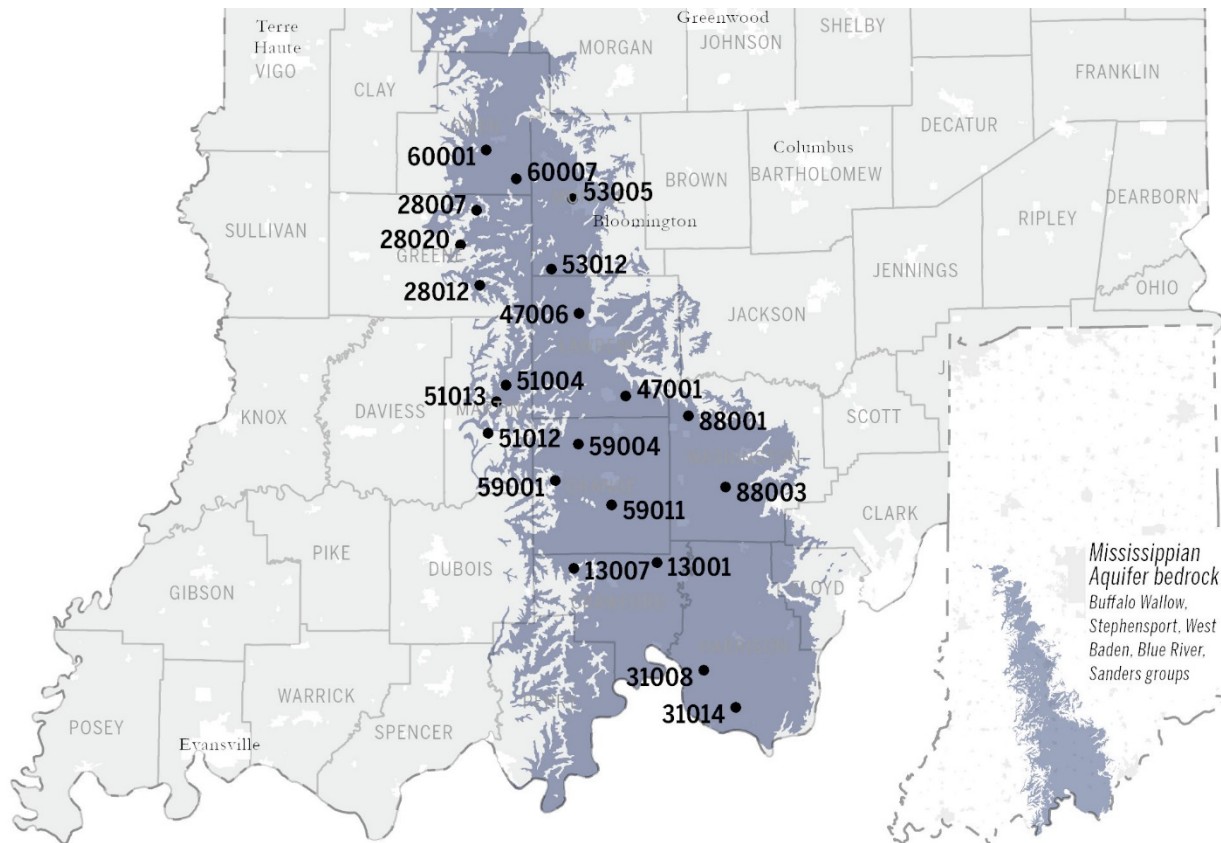


Figure 2. Map of spring locations shown with Mississippian Aquifer bedrock groups and county boundaries

No more than three and no fewer than two springs per county were sampled. A total of 26 parameters were measured, including field parameters of temperature, specific conductivity, pH, dissolved oxygen, and oxidation/reduction potential (ORP). The major ion parameters of chloride, sulfate, sodium, calcium, and potassium were determined along with alkalinity. Minor and trace elements analyzed include fluoride, nitrate, potassium, iron, manganese, zinc,

barium, strontium, silicon, arsenic, chromium, and lithium. Total dissolved solids, E. coli, and nonfecal coliform bacteria also were measured. Calculated data included bicarbonate and carbonate from alkalinity, total hardness from calcium and magnesium, Eh, the oxidation/reduction potential compared to the standard hydrogen electrode, is calculated from ORP values, and charge balance from anion and cation sums. Of these parameters, 24 are uploaded to the NGWMN site, with only E. coli and total nonfecal coliform not being included because the method used to determine these parameters is considered to be more of a screening method. Values for these parameters are included in Appendix A. All parameters were formatted in an Excel spreadsheet array appropriate for uploading to the NGWMN site, which includes project ID, site number, collection method, sampling media, sampling date, analyte name, analyte value, measure unit, sample fraction, detection limit, detection limit unit, method, and analytical method system.

Site selection approach

Several criteria were considered when selecting springs to include in the project. Of primary importance is a perennially flowing spring. This ensures that the aquifer feeding the spring is of sufficient size to allow for year-round flow. The second criterion is to make sure that the springs selected are not being recharged from a captured surface stream. The next criterion is to schedule field measurements and sampling during the dry season, to obtain a representative sample of the groundwater aquifer while minimizing potential surface recharge. A spatially distributed network of springs covering the nine targeted counties was achieved by selecting no more than three and no fewer than two springs from each county. This provides a wider coverage of springs representing both physiographic provinces in which the Mississippian bedrock aquifers occur. Accessibility to springs for sampling also was considered, such as spring proximity to access roads and permission to sample from the appropriate property owner or manager wherever necessary. A diverse selection of spring usage was considered as well, with some being used for water supplies, some for recreational/tourism attractions, and some sampled for their environmental impacts on ecosystems.

Site classification approach

Two classification systems were used for the springs. The first is based on the work conducted by Powell (1961) and covers the features identified at the spring origin, including fracture, bedding plane, and solution. Solution springs can be subdivided into cave and karst springs. The latter is identified by upwelling with no visible cave feature, often through rubble. Springs were classified based on visual observation of the spring opening. In some cases, it was impossible to identify the type of spring due to the opening being obscured by either vegetation, rubble, sediment mantling, or development features such as spring houses. Where possible, the following Powell guidelines were used for classifying springs:

1. Rock springs
 - a. Contact springs

- i. Water flowing through more permeable bedrock (sandstone, limestone, coal, etc.) overlies impermeable shale. Exits where permeable bedrock is exposed. They are also called bedding plane springs.
- b. Fracture springs
 - i. Issues from fractures or joints in bedrock, regardless of rock permeability.
- c. Solution springs. These comprise the largest group of springs, from the dissolution of carbonate rock. Two subclasses are listed below:
 - i. Cave springs
 - 1. Springs which issue from a solution channel which has its bedrock orifice above the level of the local water table.
 - ii. Karst springs
 - 1. Springs at which the resurging groundwater rises at some depth to reach the outlet at the surface.
 - 2. Are essentially cave springs buried by alluvial, glacial-fluvial, or glacial-lacustrine sediments, where water flows only after ascending through an opening.

The second classification system is based on the amount of discharge from the spring using the system devised by Meinzer (1923) (Table 1). Methods used to measure the discharge included gravity and container, Manning Equation for drainpipes, cross section and velocity, and visual estimates where actual measurements were not possible. For this project there were seven third-order magnitude springs, two fourth-order springs, eight fifth-order springs, and four sixth-order springs.

Table 1. Classification of springs by discharge (after Meinzer, 1923).

Magnitude	Average discharge cubic feet per second (ft ³ /sec)	Average discharge gallons/minute (gal/min)
1 st	100+	44,880+
2 nd	10 – 100	4,488 – 44,880
3 rd	1 – 10	448.8 – 4,488
4 th	0.22 – 1	100 – 448.8
5 th	0.02 – 0.22	10 – 100
6 th		1 – 10
7 th		0.125 – 1

Data collection techniques

Flow estimates and chemistry parameters were among the field data collected. The techniques used for flow estimates are mentioned in the previous section. Chemistry parameters measured included pH, temperature, specific conductivity, dissolved oxygen, and oxidation/reduction potential (ORP). A YSI ProDSS multiparameter sonde with datalogger was

used to collect this data. The site IDs were entered into the datalogger, configured to collect readings at one-minute intervals and left in the spring for a minimum of 5 minutes. During this time, samples were collected in 1-liter HDPE wide-mouth, screw cap bottles. Bottles were rinsed with spring water prior to filling completely full and were stored on ice until returning to the laboratory, where they were immediately forced through a stainless-steel tripod stand containing a 0.45 μm cellulose nitrate filter by a peristaltic pump. The 500 ml aliquot for measuring cations and trace metals was acidified with concentrated, high-purity nitric acid to a $\text{pH} < 2$. Both this aliquot and the filtered 250 ml aliquot for measuring anions and alkalinity were placed in a refrigerator kept at 4 $^{\circ}\text{C}$. The field chemistry on the datalogger was uploaded to the computer and the data checked for stable readings, the last of which was recorded for the spring site. The ORP measurements were converted to Eh values for the springs using the ORP method in the USGS National Field Manual (2019).

Laboratory analyses determined the alkalinity, anions, cations, minor and trace elements, and total dissolved solids. All but trace element analyses were conducted in the Indiana Geological and Water Survey water laboratory. Alkalinity was determined the next day after sampling on a Metrohm 855 Robotic Titrosampler using standardized 0.02 N (0.04 M) sulfuric acid. Samples were run in duplicate for total alkalinity determined by the first derivative of the inflection point, which was compared to the standard endpoint for alkalinity titrations of $\text{pH} 4.5$. The autosampler is capable of running ten samples in duplicate. Anions were run on a Metrohm 940 Professional IC Vario IC with 919 Autosampler Plus capable of performing 56 runs. All samples were run within 48 hours of collection. Anion analysis included fluoride, chloride, bromide, nitrite, nitrate, phosphate, and sulfate. Because no sample contained nitrite or phosphate above the instrument detection limit of 0.1 mg/L, these analytes were not included in the data set. An acceptable bromide calibration curve was never achieved, so this parameter was not reported. Major cations also were run on the Metrohm 940 and included sodium, potassium, magnesium, and calcium. Ammonia (NH_4^+) was monitored, but did not exceed the detection limit of 0.1 mg/L in any spring sample, so, as with phosphate, it was not included. Because of the stability of cations in an acidified aqueous medium, these were run in larger batches of samples covering multiple weeks of sampling, but not exceeding three weeks of storage. After major cations were completed, the acidified aliquots were delivered to the Indiana State Department of Health (ISDH) chemistry laboratory, where they were analyzed by ISDH personnel for the minor and trace elements of iron, manganese, zinc, barium, strontium, silicon, arsenic, lithium, and chromium. The two mineral springs in this project also were analyzed for nickel, primarily because of the numerous weathered coins found in the well housing of one of the springs. All elements were analyzed at the ISDH laboratory by inductively coupled plasma – mass spectrometry (ICP-MS) methods. Total dissolved solids were determined by pipetting 10 ml of filtered sample onto a pre-weighed watch glass that was then placed on a hot plate set at 70 $^{\circ}\text{C}$ in a hood, and allowed to evaporate for 48 hours, followed by additional heating at 110 $^{\circ}\text{C}$ for 24 hours. The sample plus watch glass was then weighed and the difference recorded as the total dissolved solids.

Methods for quality assurance of data

The multiple probes on the YSI ProDSS were calibrated and checked weekly to ensure that all probes were functioning correctly. The pH probe was calibrated every week using three standards of pH 4, 7, and 10. The sonde calculates a percent value for the slope calibration. If the slope deviated by more than 3% from 100%, the probe was recalibrated. If the second calibration failed, the probe was cleaned per YSI instructions. If it continued to fail, the probe was replaced. The conductivity probe was checked using a potassium chloride standard with a specific conductivity value of 1413 $\mu\text{S}/\text{cm}$. If the checked value was not within ± 10 $\mu\text{S}/\text{cm}$ of the standard value, the probe was cleaned per YSI instructions, which consists of multiple steps of cleaning and the probe being checked after each one. If it continued to fail after all cleaning steps, the probe was replaced. The oxidation/reduction probe (ORP) was checked with Zobell Solution, prepared in the laboratory, dated, and stored in an amber glass bottle. Because ORP values are temperature-dependent, the value obtained was compared to a chart with millivolt (mV) readings at various temperatures. If readings deviated by more than ± 10 mV from the standard value, a similar procedure used to clean the conductivity probe was followed. If the probe failed to achieve an acceptable reading after cleaning, it was replaced. The dissolved oxygen (DO) probe was calibrated every week using a one-point, water-saturated air value at ambient barometric pressure and temperature. Both DO percent and concentration in mg/L were recorded. A slow equilibration time was indicative of a deteriorated membrane cap, necessitating a replacement.

Raw water samples were collected at the point where spring water issued from the bedrock opening, whenever it was possible to access the opening. Some springs modified by human activity required collecting water samples from a pipe or a trough, as the actual spring opening was hidden or covered. All samples were collected in 1L high-density polyethylene (HDPE), wide-mouth, screw cap bottles that were rinsed with spring water prior to filling. Filtering was done in the IGWS lab using a procedure that included rinsing the tubing and tripod stand with 1 L ultrapure water, placing the filter, then flushing 125 ml of sample through the system to condition it for each sample and prevent carryover contamination. Aliquot bottles also were rinsed with filtered samples prior to filling. A filtration system blank was added to the samples to monitor for contaminants that may come from either the filtration unit or carryover from previous samples. If a contaminant of one of the measured components was detected in a measurable quantity, the component concentration for the springs collected after the blank was adjusted by subtracting the contaminant amount in the system blank.

The pH electrode for the alkalinity titration system was standardized with three pH calibration buffers: pH 4, 7, and 10. The electrode performance was monitored for slope accuracy and stabilization time for each buffer. The calibration program was configured to accept a slope of $100\% \pm 2\%$, and buffers had to reach stability within 60 seconds. The 0.02 N H_2SO_4 was standardized with 0.02 N NaOH, which was previously standardized against 0.02 N potassium hydrogen phthalate (KHP), a primary standard obtained from the pure salt carefully weighed

out and dissolved in a 1 L volumetric flask with ultrapure water. Each standardization consisted of three replicate titrations, and results were accepted if the relative standard deviation (RSD) was < 2%. All samples were run in duplicate, and if the RSD exceeded 2%, two more replicates were run. The value reported was obtained from the number of samples that produced an RSD < 2%, unless the absolute alkalinity values were less than 100 mg/L CaCO₃, for which an RSD < 5% was accepted. Both bicarbonate (HCO₃⁻) and carbonate (CO₃⁻²) were calculated using equations in Standard Methods (2005) that employ total alkalinity and pH for samples to determine the amount of each in units of mg CaCO₃/L, which are then converted to mg/L of HCO₃⁻ and CO₃⁻² using formula weights.

EPA method 300.1 was employed for anion analyses. The Metrohm IC was configured to use the A Supp 5 anion column with a sodium carbonate/bicarbonate eluent and a suppressor system to achieve the lowest conductivity baseline possible. The IC was calibrated using individual commercial standards that were combined in the concentrations desired for each anion. Table 2 shows the analytes measured and the concentration of each analyte in the prepared standards. A five-point calibration curve was employed for each analyte, covering the range of the majority of analyte concentrations expected. For analytes exceeding the highest value of the calibration curve, samples were diluted to bring the analyte value within the calibration range and rerun. A commercial multi-analyte check standard was run after calibration and again after samples were analyzed to verify the accuracy of the calibration curve. Duplicate runs for 20% of samples were included in each sample set. Mineral springs contained up to 20 times the high standard value for SO₄⁻² and were run undiluted to obtain values for less concentrated analytes, and run at two dilutions, 20X and 40X, to make certain the SO₄⁻² peak was quantified. All samples were run within 48 hours of collection to ensure that the nutrient anions of NO₂⁻, NO₃⁻, and PO₄⁻³ had not degraded.

Table 2. Anion standard compositions and concentrations

Analyte	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
F ⁻	0.1 mg/L	0.5 mg/L	1.0 mg/L	5.0 mg/L	10 mg/L
Cl ⁻	0.5 mg/L	2.5 mg/L	5.0 mg/L	25 mg/L	50 mg/L
Br ⁻	0.1 mg/L	0.5 mg/L	1.0 mg/L	5.0 mg/L	10 mg/L
NO ₂ ⁻	0.1 mg/L	0.5 mg/L	1.0 mg/L	5.0 mg/L	10 mg/L
NO ₃ ⁻	0.1 mg/L	0.5 mg/L	1.0 mg/L	5.0 mg/L	10 mg/L
PO ₄ ⁻³	0.1 mg/L	0.5 mg/L	1.0 mg/L	5.0 mg/L	10 mg/L
SO ₄ ⁻²	1.0 mg/L	5.0 mg/L	10 mg/L	50 mg/L	100 mg/L

Analyses for major cation chemistry employed ASTM International Method D6919-09 for alkali and alkaline earth cations by ion chromatography. This was accomplished using a second column on the Metrohm IC configured for cation analysis with a Metrosep C4 cation column and nitric acid/dipicolinic acid (NA/DPA) eluent. Cations are run in an unsuppressed system producing a high conductivity baseline with a reduction in conductivity associated with analyte

peaks. A five-point calibration curve was employed for each analyte, covering the range of expected analyte concentrations for most of the springs. The multi-analyte standards were prepared from commercial higher concentration individual analyte solutions combined in appropriate volumes using calibrated pipets and volumetric flasks to produce the calibration standards shown in Table 3. Analytes exceeding the calibration range were diluted and rerun. A commercial multi-element check standard was run after calibration and a second time after samples were run to verify the accuracy of the calibration curve. Because of the more asymmetrical shape of the analyte peaks, 60% of the samples were run in duplicate.

Table 3. Cation standard compositions and concentrations

Analyte	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Li ⁺	0.1 mg/L	0.5 mg/L	1.0 mg/L	5.0 mg/L	10 mg/L
Na ⁺	1.0 mg/L	5.0 mg/L	10 mg/L	50 mg/L	100 mg/L
NH ₄ ⁺	0.1 mg/L	0.5 mg/L	1.0 mg/L	5.0 mg/L	10 mg/L
K ⁺	0.1 mg/L	0.5 mg/L	1.0 mg/L	5.0 mg/L	10 mg/L
Ca ⁺²	1.0 mg/L	5.0 mg/L	10 mg/L	50 mg/L	100 mg/L
Mg ⁺²	0.5 mg/L	2.5 mg/L	5.0 mg/L	25 mg/L	50 mg/L

In addition to the check standards and replicates run for each analytical method, additional quality assurance procedures were employed after the major ion chemistry was completed. A charge balance equation was used to evaluate the equivalent concentrations of cations and anions. Natural waters have a net zero charge because the cations and anions are balanced. Equation 1 was employed to monitor the charge balance for spring samples.

$$(\sum_{\text{cations}} - \sum_{\text{anions}}) / (\sum_{\text{cations}} + \sum_{\text{anions}}) \times 100 = \% \text{ charge} \quad (1)$$

In this equation, each major ion is converted from mg/L to milliequivalents/L (meq/L) and added to the proper category: cations or anions. Anions incorporated into the equation include HCO₃⁻, Cl⁻, and SO₄⁻². Cations for the equation include Na⁺, Ca⁺², and Mg⁺². In cases where other ions are significant (>1 mg/L concentrations), they are incorporated into the equation, examples being F⁻, NO₃⁻, and Sr⁺². If there is an excess of cations or deficit of anions, the equation produces a positive value, and a negative value for the opposite conditions. An error of ± 5% is considered acceptable. In this way, it is possible to identify samples that have an imbalance of major components. Determining which components cause the imbalance (cations versus anions) can be ascertained using a relationship between total dissolved solids (TDS) and specific conductivity (SpC). For waters with dissolved solids less than 1000 mg/L, the ratio of TDS/SpC is typically 0.7 ± 0.1. For water samples containing more than 1000 mg/L TDS, the ratio is more variable, but typically higher, often being > 1. Ratios that significantly deviate from these values provide valuable insight to which ion group is in error. If the issue can be resolved by re-running samples, this is the procedure that is followed. In cases where components with a short holding time are involved, such as HCO₃⁻ or NO₃⁻, then re-running samples for these

components will not provide a useable value. For the first round of sampling, none of the ionic chemistry for the springs generated a charge imbalance that exceeded 4% deviation from neutral charge, as shown in Appendix A.

Description of web services

In accordance with the requirements of the National Ground Water Monitoring Network (NGWMN), it was necessary to reformat the schema of our dataset that was arranged by site (with multiple analyte samples per row). The major difference was that the new data format requires the data to be logged by sample (only one analyte per row, with multiple rows per site). Reformatting this data resulted in 300+ rows becoming 5,000+ rows. To accomplish this, the data was manipulated in Excel, then transformed and loaded into an enterprise geodatabase table using Python code.

The new schema largely follows the Environmental Protection Agency's Water Quality Exchange (WQX) format for physical/chemical data — a service that the NGWMN references in several of its own tip sheets. The data was split into two primary tables: location information and sampling data. The former is a feature class and the latter is a stand-alone table related to that feature class.

Data was loaded into an enterprise geodatabase on a locally hosted Microsoft SQL server instance. This data was published as a GIS web service powered by a locally hosted instance of ArcGIS Enterprise. A front-end application was created that allows users to search and filter data (both textually with forms and drop-downs, and spatially with a map) to learn more about the springs near them. Another component is a form built using Survey123 that allows anyone to submit the location of a spring and request a field check from IGWS researchers, at which point if it is a previously unrecorded spring, it will be added to the database and could be included in future measurements and studies.

In addition to the GIS service powering the web applications above, a separate service was published. This service was based on a subset of the data to view those specific springs that were chosen to represent the Mississippi Aquifer using the criteria described above. This service was published compliant with the Web Feature Service (WFS) protocol to allow for integration with a wider range of outside applications and data providers, including the NGWMN. This service exposes live feature-level data directly from the database in XML format.

References

ASTM D6919-09: Standard Test Method for determination of dissolved alkali and alkaline earth cations and ammonium in water and wastewater by ion chromatography, 2017. Vol. 11.02, 10 p. doi: 10.1520/D6919-09

Meinzer, O.E., 1923, The occurrence of ground water in the United States with a discussion of principles, U.S. Geological Survey Water-Supply Paper 489, Washington, D.C.

Powell, R. L., 1961., A geography of the springs of Indiana, Indiana University, M.A. thesis, 74 pp.

Standard Methods for the Examination of Water & Wastewater, 21st edition, 2005, Section 4500-CO₂ D, Carbon Dioxide and Forms of Alkalinity by Calculation, American Public Health Assoc., American Water Works Assoc., and Water Environment Federation. Washington D.C.

U.S. EPA. 1997. "Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography," Revision 1.0. Cincinnati, OH

U.S. Geological Survey National Field Manual for the Collection of Water-Quality Data, 2019, Chapter A6, Section 6.5, Reduction-Oxidation Potential (Electrode Method).

Appendix A

Table of bacteria parameters not uploaded to website and quality control parameters.

Sample ID	Anion sum meq/L	Cation sum meq/L	Charge balance \pm % dev	TDS/SpC	E. coli bacteria MPN/100 ml ^a	Nonfecal coliform bacteria MPN/100 ml ^a
13001	5.8	5.5	-2.6	0.53	40	40
13007	3.1	3.2	1.0	0.76	0	0
28007	4.9	4.9	0.0	0.75	0	0
28012	5.3	5.3	-0.6	0.76	0	40
28020	5.0	5.1	0.6	0.73	0	0
31008	6.3	6.0	-2.6	0.62	0	20
31014	6.0	5.7	-2.1	0.65	20	20
47001	6.9	6.8	-0.6	0.66	0	40
47006	6.2	6.5	2.2	0.66	60	20
51004	39.6	41.1	1.9	1.24	0	0
51012	3.8	3.8	0.1	0.75	0	0
51013	3.6	3.5	-2.2	0.68	0	20
53008	8.3	8.4	0.6	0.70	0	0
53012	5.2	5.1	-1.0	0.65	0	0
59001	65.9	60.7	-4.0	0.88	0	0
59004	7.7	7.3	-2.3	0.72	20	40
59011	4.5	4.9	3.8	0.68	0	40
60001	4.2	4.1	-0.9	0.67	0	0
60007	7.1	6.5	-3.9	0.72	20	40
88001	6.3	6.1	-1.5	0.62	0	0
88003	5.9	5.8	-1.7	0.62	20	0

^aMPN/100 ml = most probable number (of colonies) per 100 ml of sample. NOTE: bacteria samples were collected in separate 30 ml HDPE bottles and analyzed using Micrology Laboratories Coliscan® Easygel® test method.